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BOUNDARY LAYER ON A FLAT PLATE WITH SUCTION

By P. L. Bhatnagar, F.A.Sc., R. Sankar and A. C. Jain

(Department of Applied Mathematics, Indian Institute of Science, Bangalore)

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Introduction

In this paper we discuss the problem of evaluating the thickness of boundary layer and skin friction on a thin plate with suction, placed parallel to an otherwise uniform flow. A number of workers have studied this problem. For example, Blasius' classical work discusses the boundary layer on a plate at some distance from the leading edge, while Schlichting has given the solution of the problem taking into account uniform suction in which the velocity distribution is independent of the distance from the leading edge. Recently Carrier and Lin[1] have obtained the solution in the neighbourhood of the leading edge, while Torda[2] has deduced the necessary equations giving the distribution of suction at the plate which will ensure constant thickness of boundary layer. He has represented this suction velocity distribution in a graphical form for an aerofoil for which experimental data are available. We have obtained the stream function by the method of successive approximations assuming a linear law of suction which holds strictly in the neighbourhood of the leading edge. In passing, we may mention that in the absence of suction the present solution reduces to a form similar to that given by Carrier and Lin. We have obtained the thickness of the boundary layer and the skin friction explicitly in terms of suction velocity and distance from the leading edge without putting any restriction on the distribution of suction speed on the plate. To ensure symmetry we have assumed the suction to take place with the same speed at the corresponding points on the two sides of the plate.

It is evident that our aim is in a sense different from that of Torda. While Torda has attempted to specify the distribution of suction speed over the plate to ensure a constant thickness of boundary layer, we have attempted to evaluate the boundary layer thickness in terms of a specified distribution of suction speed. The present point of view may be found more useful in practice besides being more general than that of Torda.

The explicit expressions for velocity boundary layer thickness $\delta(x)$ and the skin friction $\tau_0(x)$ for the downstream flow as obtained in this paper are:

$$\delta(x) = \frac{\sqrt{x}}{a} + \frac{v_0(x)}{2}\left(\frac{\sqrt{x}}{a}\right)^2 + \left\{\frac{1}{48} + \frac{v_0^2(x)}{3}\right\}\left(\frac{\sqrt{x}}{a}\right)^3 + \frac{v_0^3(x)}{4}\left(\frac{\sqrt{x}}{a}\right)^4 + \ldots,$$

and

$$\tau_0(x) = \mu\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)_{y=0} = \mu\left(\frac{a}{\sqrt{x}} - v_0'(x)\right),$$

where

$$a = 0{\cdot}332.$$

1. Description of the Flow Near the Leading Edge

The equations governing an incompressible, viscous, fluid flow in two-dimensional cartesian co-ordinates x_1, y_1 are:

Equation of continuity:

$$\frac{\partial u_1}{\partial x_1} + \frac{\partial v_1}{\partial y_1} = 0, \tag{1.1}$$

Equations of momentum:

$$u_1\frac{\partial u_1}{\partial x_1} + v_1\frac{\partial u_1}{\partial y_1} + \frac{1}{\rho}\frac{\partial p_1}{\partial x_1} = \nu\nabla^2 u_1, \tag{1.2}$$

$$u_1\frac{\partial v_1}{\partial x_1} + v_1\frac{\partial v_1}{\partial y_1} + \frac{1}{\rho}\frac{\partial p_1}{\partial y_1} = \nu\nabla^2 v_1. \tag{1.3}$$

The introduction of the following dimensionless variables:

$$p = \frac{p_1}{\frac{1}{2}\rho u_0^2}, \quad x = \frac{x_1 u_0}{\nu}, \quad y = \frac{y_1 u_0}{\nu}, \quad u = \frac{u_1}{u_0} = \frac{\partial\psi}{\partial y},$$

$$v = \frac{v_1}{v_0} = -\frac{\partial\psi}{\partial x}, \tag{1.4}$$

where u_0 is the free stream velocity, reduces the above equations to:

$$\nabla^4\psi = \frac{\partial\psi}{\partial y}\frac{\partial}{\partial x}(\nabla^2\psi) - \frac{\partial\psi}{\partial x}\frac{\partial}{\partial y}(\nabla^2\psi), \tag{1.5}$$

where

$$\nabla^2\psi \equiv \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}. \tag{1.6}$$

It is found convenient to work through polar co-ordinates defined by

$$x = r\cos\theta, \quad y = r\sin\theta.$$

With these, (1.5) and (1.6) reduce to:

$$\frac{\partial^4\psi}{\partial r^4} + \frac{2}{r}\frac{\partial^3\psi}{\partial r^3} - \frac{1}{r^2}\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r^3}\frac{\partial\psi}{\partial r} + \frac{2}{r^2}\left(\frac{\partial^4\psi}{\partial r^2\partial\theta^2} - \frac{1}{r}\frac{\partial^3\psi}{\partial r\partial\theta^2} + \frac{2}{r^2}\frac{\partial^2\psi}{\partial\theta^2}\right) + \frac{1}{r^4}\frac{\partial^4\psi}{\partial\theta^4}$$

$$= \frac{1}{r}\left\{\frac{\partial\psi}{\partial\theta}\frac{\partial}{\partial r}(\nabla^2\psi) - \frac{\partial\psi}{\partial r}\frac{\partial}{\partial\theta}(\nabla^2\psi)\right\}, \tag{1.7}$$

where

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial\theta} + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2}. \tag{1.8}$$

Following Carrier and Lin we write this equation as

$$\mathbf{L}(\psi) = \mathbf{L}^*(\psi), \tag{1.9}$$

where $\mathbf{L}$ denotes the biharmonic operator and $\mathbf{L}^*$ denotes the non-linear operator on the right. For a linear law of suction,

$$v(x, 0) = -\mathrm{V}x, \tag{1.10}$$

the boundary conditions are

$$\left.\begin{aligned} \left(\frac{\partial\psi}{\partial r}\right)_{\theta=0} &= \mathrm{V}r, & \left(\frac{\partial\psi}{\partial r}\right)_{\theta=2\pi} &= -\mathrm{V}r, \\ \left(\frac{\partial\psi}{r\partial\theta}\right)_{\theta=0} &= 0, & \left(\frac{\partial\psi}{r\partial\theta}\right)_{\theta=2\pi} &= 0 \end{aligned}\right\}. \tag{1.11}$$

We assume a solution of (1.9) in the form:

$$\psi = \psi_0 + \psi_1 + \psi_2 + \ldots, \tag{1.12}$$

where

$$\psi_0, \psi_1, \psi_2, \ldots,$$

are defined by

$$\mathrm{L}(\psi_0) = 0, \tag{1.13 a}$$

$$\mathrm{L}(\psi_1) = \mathrm{L}^*(\psi_0), \tag{1.13 b}$$

$$\mathrm{L}(\psi_2) = \mathrm{L}^*(\psi_0 + \psi_1) - \mathrm{L}^*(\psi_0), \tag{1.13 c}$$

.....

$$\mathrm{L}(\psi_n) = \mathrm{L}^*(\psi_0 + \psi_1 + \ldots + \psi_{n-1}) - \mathrm{L}^*(\psi_0 + \psi_1 + \ldots + \psi_{n-2}), \tag{1.13 n}$$

We shall choose ψ_0 such that it satisfies the boundary conditions (1.11) completely, *i.e.*,

$$\left.\begin{aligned} \left(\frac{\partial \psi_0}{\partial r}\right)_{\theta=0} &= \mathrm{V}r, & \left(\frac{\partial \psi_0}{\partial r}\right)_{\theta=2\pi} &= -\mathrm{V}r, \\ \left(\frac{\partial \psi_0}{\partial \theta}\right)_{\theta=0} &= 0, & \left(\frac{\partial \psi_0}{\partial \theta}\right)_{\theta=2\pi} &= 0 \end{aligned}\right\}. \tag{1.14}$$

Besides the velocity distribution (as determined by ψ_0) is to be symmetric about the plate. The boundary conditions to be satisfied by ψ_i for $i > 0$, are

$$\frac{\partial \psi_i}{\partial r} = \frac{\partial \psi_i}{\partial \theta} = 0, \quad \text{at} \quad \theta = 0, \quad 2\pi. \tag{1.15}$$

Also the velocity distribution (as determined from each one of the ψ_i's) is to be symmetrical about the plate.

The first two conditions in (1.14) suggest a solution for (1.13 *a*) in the form

$$\psi_0 = r^2 f(\theta). \tag{1.16}$$

Using this form we find that $f(\theta)$ has to satisfy

$$f^{\mathrm{IV}} + 4f'' = 0, \tag{1.17}$$

with the conditions

$$\left.\begin{aligned} f(0) &= \frac{\mathrm{V}}{2}, & f(2\pi) &= -\frac{\mathrm{V}}{2}, \\ f'(0) &= 0, & f'(2\pi) &= 0. \end{aligned}\right\} \tag{1.18}$$

With these we easily see that the solution of (1.13 *a*) of the assumed type is

$$\psi_0 = \frac{Vr^3}{2} + \frac{Vr^2}{4\pi}(\sin 2\theta - 2\theta) - 2Cr^3 \sin^3\theta, \tag{1.19}$$

where the constant C is yet undetermined.

The symmetry of velocity distribution demands

$$\left.\begin{aligned} \left(\frac{\partial\psi_0}{r\partial\theta}\right)_{\substack{r=\rho \\ \theta=\alpha}} &= \left(\frac{\partial\psi_0}{r\partial\theta}\right)_{\substack{r=\rho \\ \theta=2\pi-\alpha}}, \\ \left(\frac{\partial\psi_0}{\partial r}\right)_{\substack{r=\rho \\ \theta=\alpha}} &= -\left(\frac{\partial\psi_0}{\partial r}\right)_{\substack{r=\rho \\ \theta=2\pi-\alpha}}, \end{aligned}\right\} \tag{1.20}$$

for all ρ and α.

These conditions yield

$$C = 0. \tag{1.21}$$

Thus

$$\psi_0 = \frac{Vr^2}{2} + \frac{Vr^2}{4\pi}(\sin 2\theta - 2\theta). \tag{1.22}$$

If we put $V = 0$ in (1.22), we get,

$$\psi_0 \equiv 0. \tag{1.23}$$

Hence we find that the above stream function is unable to account for the flow without suction.

The boundary conditions for the flow without suction are

$$\left.\begin{aligned} \left(\frac{\partial\psi}{\partial r}\right)_{\theta=0} &= 0, \quad \left(\frac{\partial\psi}{\partial r}\right)_{\theta=2\pi} = 0, \\ \left(\frac{\partial\psi}{\partial\theta}\right)_{\theta=0} &= 0, \quad \left(\frac{\partial\psi}{\partial\theta}\right)_{\theta=2\pi} = 0. \end{aligned}\right\} \tag{1.24}$$

Besides the velocity distribution is to be symmetric about the plate. It is found by trial that the least value of n for which a function of the form $r^n f(\theta)$ satisfies these conditions is 3/2 and the corresponding function $f(\theta)$ is given by

$$f(\theta) = \cos\frac{\theta}{2} - \cos\frac{3\theta}{2}. \tag{1.25}$$

Thus to get a complete expression for ψ_0 which will also account for the flow in the absence of suction without affecting the boundary conditions we must add to (1.22).

$$2Ar^{3/2}\left(\cos\frac{\theta}{2} - \cos\frac{3\theta}{2}\right), \tag{1.26}$$

where A is yet an undetermined constant which is independent of suction.

Hence

$$\psi_0 = \frac{Vr^2}{2} + \frac{Vr^2}{4\pi}(\sin 2\theta - 2\theta) + 2Ar^{3/2}\left(\cos\frac{\theta}{2} - \cos\frac{3\theta}{2}\right). \tag{1.27}$$

The presence of the constant A allows us a choice to fix up the flow without suction.

With this value of ψ_0, (1.13 *b*) becomes

$$\begin{aligned} L(\psi_1) = {} & \frac{2A^2}{r}(2\sin\theta - 3\sin 2\theta) \\ & + \frac{AV}{\pi r^{1/2}}\left(2\pi\sin\frac{\theta}{2} + 7\cos\frac{\theta}{2} - 2\theta\sin\frac{\theta}{2} - 6\cos\frac{3\theta}{2}\right. \\ & \left. - \cos\frac{5\theta}{2}\right) \\ & + \frac{2V^2}{\pi}\left(1 - \frac{\theta}{\pi} + \frac{1}{2\pi}\sin 2\theta\right) \end{aligned} \tag{1.28}$$

It appears that a solution of (1.28) is of the form

$$\psi_1 = r^3 f_1(\theta) + r^{7/2} f_2(\theta) + r^4 f_3(\theta); \tag{1.29}$$

but such a solution is found not to satisfy boundary conditions (1.15) and the symmetry conditions unless $V = 0$. Thus we cannot proceed with the above form of solution for ψ_1 if we are interested in a solution for the problem with suction. It is found that a function of the form

$$\begin{aligned} \psi_1 = {} & A^2 r^3 \{f_1(\theta) + \phi_1(\theta)\log r\} \\ & + \frac{AV}{\pi} r^{7/2}\{f_2(\theta) + \phi_2(\theta)\log r\} \end{aligned}$$

$$+\frac{2V^2}{\pi}r^4\{f_3(\theta)+\phi_3(\theta)\log r\}, \tag{1.30}$$

satisfies (1.28) and the conditions (1.15) along with the symmetry of the velocity distribution. Using this we find that f_1, f_2, f_3, ϕ_1, ϕ_2, ϕ_3 have to satisfy

$$\phi_1^{IV}+10\phi_1''+9\phi_1=0, \tag{1.31}$$

$$f_1^{IV}+10f_1''+9f_1=-24\phi_1-8\phi_1''+4\sin\theta-6\sin 2\theta, \tag{1.32}$$

$$\phi_2^{IV}+\frac{29}{2}\phi_2''+\frac{441}{16}\phi_2=0, \tag{1.33}$$

$$f_2^{IV}+\frac{29}{2}f_2''+\frac{441}{16}f_2=-\frac{105}{2}\phi_2-10\phi_2''+2\pi\sin\frac{\theta}{2}+7\cos\frac{\theta}{2}-2\theta\sin\frac{\theta}{2}-6\cos\frac{3\theta}{2}-\cos\frac{5\theta}{2}, \tag{1.34}$$

$$\phi_3^{IV}+20\phi_3''+64\phi_3=0, \tag{1.35}$$

$$f_3^{IV}+20f_3''+64f_3=-96\phi_3-12\phi_3''+1-\frac{\theta}{\pi}+\frac{1}{2\pi}\sin 2\theta, \tag{1.36}$$

with the conditions

$$\left.\begin{aligned} f_i(0)=f_i(2\pi)=f_i'(0)=f_i'(2\pi)=0,\\ \phi_i(0)=\phi_i(2\pi)=\phi_i'(0)=\phi_i'(2\pi)=0,\\ i=1,\ 2,\ 3.\end{aligned}\right\} \tag{1.37}$$

These equations admit of direct solution and we get

$$\psi_1=Ar^2\left[\frac{\pi-\theta}{8}(\cos 3\theta-\cos\theta)+\frac{2}{5}(\sin 2\theta-2\sin\theta)+\frac{1}{8}(3\sin\theta-\sin 3\theta)\log\kappa r\right]$$
$$+\frac{AV}{\pi}r^{7/2}\left[\frac{1}{144}\left(49\cos\frac{\theta}{2}+6\cos\frac{5\theta}{2}-55\cos\frac{7\theta}{2}\right)+\frac{\pi-\theta}{240}\left(20\sin\frac{\theta}{2}+89\sin\frac{3\theta}{2}-41\sin\frac{7\theta}{2}\right)+\frac{41}{240}\left(\cos\frac{3\theta}{2}-\cos\frac{7\theta}{2}\right)\log\lambda r\right]$$

$$+\frac{V^2}{96\pi^2}r^4[(\pi-\theta)(3-8\cos 2\theta+5\cos 4\theta)$$

$$+5(2\sin 2\theta-\sin 4\theta)\log \mu r], \tag{1.38}$$

where κ, λ, μ are constants yet undetermined.

It is difficult to find the domain of convergence of the series

$$\psi_0+\psi_1+\psi_2+\ldots$$

But the formation of the terms show that there exists a circle of convergence for the series.

2. DETERMINATION OF THE CONSTANT A

In the case of no suction, *i.e.*, $V=0$, the stream function is given by

$$\bar{\psi}=2Ar^{3/2}\left(\cos\frac{\theta}{2}-\cos\frac{3\theta}{2}\right)$$

$$+A^2r^3\left[\frac{\pi-\theta}{8}(\cos 3\theta-\cos\theta)+\frac{2}{5}(\sin 2\theta-2\sin\theta)\right.$$

$$\left.+\frac{1}{8}(3\sin\theta-\sin 3\theta)\log \kappa r\right] \tag{2.1}$$

So for small values of θ the velocity u is given by

$$u\simeq 4Ar^{1/2}\theta+\frac{8}{3}Ar^{1/2}\theta^3+A^2r^2\left[-\pi\theta+\frac{3}{10}(1+5\log r)\theta^2\right.$$

$$\left.+\frac{2}{3}\pi\theta^3-\left(\frac{14}{15}+\frac{1}{2}\log r\right)\theta^4\right]+\ldots, \tag{2.2}$$

The velocity profile obtained by Blasius for flow downstream is given by

$$u=a\eta-\frac{a^2\eta^4}{2.4!}+\ldots, \tag{2.3}$$

where

$$\eta=\frac{y}{x^{1/2}} \quad \text{and} \quad a=0{\cdot}332.$$

For small values of r and θ,

$$u\simeq ar^{1/2}\theta-\frac{a^2r^2\theta^4}{48}+\ldots, \tag{2.4}$$

For sufficiently small values of r and θ the leading term of the expansion describes the flow. Hence comparing the coefficients of $r^{1/2}\theta$ in the above expansions (2.2) and (2.4) we get

$$4A = a = 0{\cdot}332.$$

Therefore

$$A = 0{\cdot}083. \tag{2.5}$$

Now that A is found we can calculate the vorticity ζ and skin friction τ_0.

We get

$$\begin{aligned}\zeta = &-\frac{2V}{\pi}(\pi-\theta) - \frac{4A}{r^{1/2}}\cos\frac{\theta}{2} \\ &+ A^2 r\left\{(\pi-\theta)\cos\theta + \frac{22}{5}\sin\theta + 2\sin 2\theta \right. \\ &\quad \left. + 3(\sin\theta)\log \kappa r\right\} \\ &- \frac{AV}{\pi} r^{3/2}\left\{\left(\pi-\theta\right)\left(\sin\frac{\theta}{2} + \frac{89}{24}\sin\frac{3\theta}{2}\right) + 4\cos\frac{\theta}{2}\right. \\ &\quad \left. + \frac{1}{12}\cos\frac{3\theta}{2} + \frac{1}{4}\cos\frac{5\theta}{2} + \frac{41}{24}\left(\cos\frac{3\theta}{2}\right)\log \lambda r\right\} \\ &- \frac{V^2 r^2}{2\pi^2}\left\{(\pi-\theta)(1-2\cos 2\theta) + \sin 2\theta\right. \\ &\quad \left. + \frac{5}{2}(\sin 2\theta)\log \mu r\right\}. \end{aligned} \tag{2.6}$$

The skin friction in the case of continuously varying suction is given by,

$$\tau_0 = \mu\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)_{y=0}. \tag{2.7}$$

Hence we get

$$\tau_0 = \mu\left[\frac{a}{x^{1/2}} - \frac{a^2\pi x}{16} + \frac{aV}{12\pi}x^{3/2}\left(13 + \frac{41}{8}\log \lambda x\right) - \frac{1}{2}\frac{V^2x^2}{\pi}\right]. \tag{2.8}$$

3. Description of the Flow Downstream

In the downstream region the Navier Stokes equations in the dimensionless form are represented approximately by the boundary layer equation

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\frac{\partial^2 u}{\partial y^2}, \tag{3.1}$$

along with the equation of continuity (1.1). The boundary conditions to be satisfied are

$$\left.\begin{aligned} &u=0, \quad v=-v_0(x), \quad \text{at} \quad y=0, \\ &\text{and} \\ &u\to 1, \qquad\qquad\quad \text{as} \quad y\to\infty, \end{aligned}\right\} \tag{3.2}$$

where $v_0(x)$ is the suction speed.

To solve this equation we assume a stream function

$$\psi=\sum_{n=0}^{\infty} a_n(x)\,y^n, \tag{3.3}$$

The first two of the boundary conditions (3.2) give

$$a_0'(x)=v_0(x), \quad a_1(x)=0. \tag{3.4}$$

Substituting ψ from (3.3) in (3.1) we get,

$$a_3(x)=-\tfrac{1}{3}v_0(x)\,a_2(x), \tag{3.5}$$

$$a_4(x)=\frac{1}{12}v_0^2(x)\,a_2(x), \tag{3.6}$$

with the general recurrence relation

$$a_{n+3}(x)=-\frac{1}{n+3}v_0(x)\,a_{n+2}(x)+\frac{1}{(n+1)(n+2)(n+3)} \times\sum_{r=2}^{n}(n+3-2r)\,ra_r(x)\,a'_{n+2-r}(x), \quad n>1, \tag{3.7}$$

From the recurrence relation, we get

$$a_5(x)=-\frac{1}{60}v_0^3(x)\,a_2(x)+\frac{1}{30}a_2'(x)\,a_2(x), \tag{3.8}$$

$$a_6(x)=-\frac{1}{360}v_0^4(x)\,a_2(x)-\frac{1}{60}v_0(x)\,a_2(x)\,a_2'(x) -\frac{1}{90}v_0'(x)\,a_2^2(x), \tag{3.9}$$

$$a_7(x) = \frac{-1}{2520} v_0^5(x) a_2(x) + \frac{1}{210} v_0^2(x) a_2(x) a_2'(x)$$

$$+ \frac{1}{126} v_0(x) v_0'(x) a_2^2(x), \tag{3.10}$$

$a_2(x)$ is left undetermined. This is as to be expected since one boundary condition, *viz.*,

$$u \to 1 \quad \text{as} \quad y \to \infty.$$

has not been used so far.

u, as determined from (3.3), is

$$u = 2a_2(x) y + 3a_3(x) y^2 + \ldots, \tag{3.11}$$

We determine $a_2(x)$ by comparing the leading terms in the present velocity profile with $v_0(x) = 0$ and the Blasius' solution (2.3).

From (2.3) we get

$$u = \frac{\alpha y}{x^{1/2}} - \frac{\alpha^2}{2.4!} \frac{y^4}{x^2} + \ldots, \tag{3.12}$$

Equating the coefficients of y from (3.12) and (3.13) we get

$$a_2(x) = \frac{\alpha}{2x^{1/2}}, \quad \text{where } \alpha = 0{\cdot}332. \tag{3.13}$$

With this value of $a_2(x)$, if we put $v_0(x) = 0$ throughout the series, we get the Blasius solution.

Now that $a_2(x)$ is known we get

$$a_3(x) = -\frac{\alpha}{6x^{1/2}} v_0(x), \tag{3.14}$$

$$a_4(x) = \frac{\alpha}{24x^{1/2}} v_0^2(x), \tag{3.15}$$

$$a_5(x) = -\frac{\alpha}{120x^{1/2}} v_0^3(x) - \frac{\alpha^2}{240x^2}, \tag{3.16}$$

$$a_6(x) = \frac{\alpha}{720x^{1/2}} v_0^4(x) + \frac{\alpha^2}{480x^2} v_0(x) - \frac{\alpha^2}{360x} v_0'(x), \tag{3.17}$$

$$a_7(x) = -\frac{a}{5040x^{1/2}}v_0^5(x) - \frac{a^2}{1680x^2}v_0^2(x) + \frac{a^2}{504x}v_0(x)v_0'(x), \tag{3.18}$$

$a_8(x)$, $a_9(x)$, etc., can be similarly calculated. With the use of these values we get

$$u = \frac{a}{x^{1/2}}y - \frac{av_0(x)}{2x^{1/2}}y^2 + \frac{av_0^2(x)}{6x^{1/2}}y^3 - \left(\frac{av_0^3(x)}{24x^{1/2}} + \frac{a^2}{48x^2}\right)y^4 + \left(\frac{av_0^4(x)}{120x^{1/2}} + \frac{a^2v_0(x)}{80x^2} - \frac{a^2v_0'(x)}{60x}\right)y^5 - \left(\frac{av_0^5(x)}{720x^{1/2}} + \frac{a^2v_0^2(x)}{240x^2} - \frac{a^2v_0(x)v_0'(x)}{72x}\right)y^6 + \ldots\ldots\ldots\ldots, \tag{3.19}$$

Using Lagrange's reversion formula we get

$$y = \frac{\sqrt{x}}{a}u + \frac{v_0(x)}{2}\left(\frac{\sqrt{x}}{a}\right)^2u^2 + \frac{v_0^2(x)}{3}\left(\frac{\sqrt{x}}{a}\right)^3u^3 + \left\{\frac{v_0^3(x)}{4}\left(\frac{\sqrt{x}}{a}\right)^4 + \frac{1}{48}\left(\frac{\sqrt{x}}{a}\right)^3\right\}u^4 + \ldots, \tag{3.20}$$

Since at the edge of the boundary layer the velocity is approximately the free stream velocity we have

$$u \simeq 1, \quad \text{at} \quad y = \delta. \tag{3.21}$$

Hence

$$\delta(x) \simeq \frac{\sqrt{x}}{a} + \frac{v_0(x)}{2}\left(\frac{\sqrt{x}}{a}\right)^2 + \frac{v_0^2(x)}{3}\left(\frac{\sqrt{x}}{a}\right)^3 + \left\{\frac{v_0^3(x)}{4}\left(\frac{\sqrt{x}}{a}\right)^4 + \frac{1}{48}\left(\frac{\sqrt{x}}{a}\right)^3\right\} + \ldots, \tag{3.22}$$

Thus an explicit analytic expression for $\delta(x)$ has been derived valid for any suction velocity distribution. The authors are not aware of any explicit expression having been given earlier by anyone.

The skin friction τ_0 is given by

$$\tau_0(x) = \mu\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)_{y=0} = \mu\left(\frac{a}{\sqrt{x}} - v_0'(x)\right). \tag{3.23}$$

The solution near the leading edge has been given only for a linear law of suction, but from the method it is clear that any other power law can be used. Or in general any suction law can be dealt with by using the power series expansion for the function. The detailed solution for the leading edge with any suction is being worked out.*

Summary

In this paper we have discussed the boundary layer on a plate with suction. The problem is solved near the leading edge as well as far downstream. A linear suction law is assumed near the leading edge for simplicity, whereas no restriction is placed on the suction law in the region downstream. An explict expression for boundary layer thickness in terms of suction speed and distance from leading edge is derived. It is found that the thickness of the boundary layer depends on the derivative of the suction speed. The skin friction also has been evaluated. Though near the leading edge a linear law of suction is assumed, the method used in the paper can be easily generalised for any other power law, for example, we may use a power series expansion for the function defining the suction velocity.

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2. Torda, T. P. .. *Jour. Math. and Physics*, 1952, **31**, 206.

* One of the authors (A. C. J.) has found out the solution at the leading edge with constant suction and his solution will be published in a separate paper along with other results.

EMISSION SPECTRUM OF BISMUTH MONOCHLORIDE

Part I. The Vibrational Analysis of the 6170-4220 Å System*

By Putcha Venkateswarlu, F.A.Sc. and Baij Nath Khanna

(Department of Physics, Muslim University, Aligarh)

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Abstract

Bismuth chloride has been excited in flowing condition with an uncondensed transformer discharge. About 390 bands are observed in the present experiments of which only 140 were recorded by earlier workers. The vibrational constants obtained are the same as those obtained by Morgan from absorption experiments except for the addition of a cubic term for the upper state. It appears quite likely that the upper state of the system dissociates into Bi ($^4S_{3/2}$) + Cl ($^2P_{1/2}$) while the lower state, which is probably the ground state, dissociates into Bi ($^4S_{3/2}$) + Cl ($^2P_{3/2}$). The rough values of the dissociation energies obtained by extrapolations are $D_0' = 3750$ cm.$^{-1}$ and $D_0'' = 24614$ cm.$^{-1}$

Introduction

Visible bands in the region 4300–5400 Å attributed to bismuth monochloride are well known from a long time back. Saper[1] excited the vapour of bismuth trichloride in active nitrogen and analysed the bands in the region 4300–5400 Å as emitted by the diatomic bismuth monochloride molecule. His analysis was confirmed by the observed isotopic shifts which tallied fairly well with those calculated from the BiCl molecule. Ghosh,[2] however, rephotographed the bands lying in the region 4300–6600 Å by feeding carbon arc with metallic bismuth or bismuth trichloride and attributed them to the BiO molecule. Morgan[3] studied bismuth halides extensively by taking absorption spectrum of all of them. Halogens were passed over molten mass of bismuth which was placed inside the furnace heated up to 900–1400° C. He obtained all the systems also by placing different bismuth halides inside the furnace. Two systems one in the region 5400–4300 Å and the other lying in the region 4000–3600 Å were obtained in the bismuth monochloride

* This forms part of the Ph.D. thesis submitted by B. N. K. to M.U., Aligarh.

molecule. He observed the isotopic shifts of the right magnitude for the band heads of BiCl and BiBr molecules. The presence of the isotopic shifts as well as the presence of analogous systems in all the halides led him to conclude that these bands are due to bismuth halides.

Ray[4] further studied the spectrum of bismuth monochloride in absorption and also in emission by feeding carbon arc with bismuth trichloride. He confirmed the formula proposed by Morgan[3] for the less refrangible system and showed that the emitter of the system is BiCl molecule.

However, in the experiments of all the workers mentioned above, there was a possibility of the presence of different impurities as the experiments were conducted in the open atmosphere. Therefore, it was felt necessary to obtain these bands using a discharge tube avoiding the presence of atmospheric gases and thus to give a better experimental proof for them. As no rotational structure was observed and analysed so far for this molecule, it was expected that such a work will help us to determine the rotational constants and the electronic transitions involved. Further it was also expected that the transformer discharge might give larger number of new bands which might help us to extend and improve the vibrational analysis.

The experiments performed were found to be quite successful to develop the system 6170–4220 Å extensively and the present paper deals with the vibrational analysis of the bands so developed. The rotational analysis of some of these bands will be discussed in the next paper.

Experimental Details

The discharge tube, having cylindrical nickel electrodes placed coaxially along its length, was 0·8 cm. in diameter and 40 cm. in length. It was continuously pumped out from one end through a stopcock whereas at the other end a side tube containing bismuth trichloride was attached. Since $BiCl_3$ is hygroscopic, it was dehydrated completely before starting the experiment.

The vapour was excited by an uncondensed transformer discharge applying 15 K.V. with a Hilger ¼ K.W. power transformer. The discharge tube near the electrodes as well as the side tubes containing the sample were heated continuously by a Bunsen burner so as to maintain a sufficient high pressure of the vapour. The samples obtained from two different sources, *i.e.*, B.D.H. and E. Merck were tried. The colour of the discharge was intense greenish-blue. Only one system lying in the region 6170–4220 Å was obtained. The other system, that was obtained by the earlier workers on the shorter wavelength side of this system, was not excited in the present experiments.

The spectrum was first taken on a Zeiss three-prism glass spectrograph having a dispersion of 11·4 Å/mm. at 4800 Å and then on the first and second

TABLE I

Wavelengths, wavenumbers and relative intensities of the band system 6170–4220 *Å of BiCl*

λ_{air}	I	$\nu_{vac.}$	λ_{air}	I	$\nu_{vac.}$
6173·4	2	16194	43·3	2	17109
6093·6	2	16406	39·8	4	17119
88·4	2	16420	35·1	2	17133
79·2	2	16445	30·6	1	17146
69·2	1	16472	26·6	0	17158
65·9	1	16481	21·5	1	17173
57·8	1	16503	12·7	4	17199
51·6	0	16520	11·3	6	17203
45·7	1	16536	05·3	2	17221
10·5	0	16633	5799·8	2	17237
02·2	2	16656	95·5	1	17250
5997·5	1	16669	91·1	1	17263
94·3	3	16678	84·8	1	17282
89·2	1	16692	79·1	4	17299
73·5	2	16736	75·1	2	17311
69·6	2	16747	66·4	1	17337
67·4	2	16753	59·8	1	17357
63·2	3	16765	55·1	1	17371
58·9	1	16777	50·2	4	17386
55·3	1	16787	46·9	1	17396
49·3	1	16804	5736·6	2	17427
43·0	1	16822	32·0	1	17441
38·4	1	16835	23·8	1	17466
35·2	1	16844	19·5	5	17479
30·6	3	16857	08·5	1	17513
25·0	1	16873	02·6	1	17531
20·1	1	16887	5695·4	3	17553
15·9	1	16899	90·6	5	17568
5908·9	3	16919	89·0	3	17573
01·6	5	16940	69·3	2	17634
5893·2	1	16964	61·6†	5	17658
83·1	2	16993	48·8	1	17698
76·2	0	17013	37·6	?	17733
71·4	2	17027	33·2†	6	17747
69·3	4	17033	20·5	?	17787
64·5	2	17047	05·1†	6	17836
55·6	1	17073	5599·7	1	17856
46·0	2	17101	95·7	1	17866_8

TABLE I (*Contd.*)

λ_{air}	I	$\nu_{vac.}$	λ_{air}	I	$\nu_{vac.}$
81·3	2	17912$_g$	5346·8	0	18698$_g$
79·1†	?	17919$_g$	45·0†	3	18704$_g$
76·0†	6	17929$_g$	35·8	2	18736$_g$
72·6	0	17940$_g$	31·0*	4	18753$_g$
64·5	2	17966$_g$	26·5	1	18679
57·1	0	17990	12·6†	1	18818$_g$
51·2	1	18009$_g$	08·9	2	18831$_g$
48·2†	5	18019$_g$	07·2*	5	18837$_g$
36·5	1	18057$_g$	03·8†	2	18849$_g$
32·5	1	18070	5298·8	1	18867$_g$
27·6	1	18086$_g$	89·3†	2	18901
21·5†	6	18106$_g$	84·8*	4	18917$_g$
12·1	2	18137$_g$	76·4*	2	18947$_g$
5509·4	0	18146$_g$	66·4†	1	18983$_g$
00·5	1	18175$_g$	63·3*	2	18994$_g$
5496·0†	4	18190$_g$	51·5*	4	19037$_g$
92·1†	2	18203$_g$	46·0	0	19057$_g$
87·9	0	18217	42·7	1	19069$_g$
82·1	1	18236$_g$	34·1	1	19100
71·3†	4	18272$_g$	32·5	1	19106$_g$
68·9	0	18280$_g$	28·1*	5	19122$_g$
67·7	0	18284$_g$	14·7	?	19171$_g$
65·1	2	18293$_g$	12·3†	1	19180
64·2†	5	18296$_g$	05·8*	3	19204$_g$
52·8	1	18334$_g$	01·7	3	19219$_g$
49·0†	2	18347$_g$	5198·0	2	19233
43·6	2	18365$_g$	90·7*	2	19260
37·7†	6	18385$_g$	86·7	2	19275$_g$
27·1	1	18421$_g$	83·9*	4	19285$_g$
19·4	2	18447$_g$	79·1	2	19303$_g$
15·6	2	18460$_g$	75·3*	3	19317$_g$
12·7†	4	18470$_g$	5169·2†	1	19340
09·5	2	18481$_g$	64·1*	2	19359
06·8	1	18524$_g$	59·9	2	19375
5397·0	?	18490$_g$	50·8*	4	19409$_g$
91·2	2	18544$_g$	49·2	1	19415$_g$
88·5*	3	18553$_g$	47·6	0	19421$_g$
82·4†	2	18574$_g$	40·0	2	19450$_g$
75·1	1	18599$_g$	36·5†	0	19463$_g$
71·8	1	18611$_g$	28·4*	6	19494$_g$
69·1	1	18620$_g$	24·2	2	19510$_g$
67·4	2	18626$_g$	20·7†	0	19523
65·6†	2	18632	15·0*	4	19545$_g$
61·6	0	18646$_g$	09·2	1	19567$_g$
56·1†	4	18665$_g$	07·4*	8	19574$_g$

TABLE I (*Contd.*)

λ_{air}	I	$\nu_{vac.}$	λ_{air}	I	$\nu_{vac.}$
5098·2†	1	19609	66·5*	8	20543
94·6†	2	19623	63·4	1	20556
91·3	2	19636	60·1*	2	20570
87·1*	4	19652	59·4	2	20573
74·7*	1	19700	58·7*	2	20576
68·8	1	19723	56·3	1	20586
53·7*	3	19782	52·5†	1	20602
48·8*	2	19801	43·1	1	20642
41·5†	1	19830	37·3*	3	20667
36·9	0	19848	34·5	1	20679
32·3*	7	19866	33·3	0	20684
27·7	1	19884	31·2†	1	20693
24·7*	2	19896	29·1	0	20702
21·2*	3	19910	27·0	1	20711
15·2	1	19934	17·9	2	20750
11·6*	5	19948	15·6†	1	20760
5008·4	1	19961	12·8	1	20772
01·1*	3	19990	10·7†	1	20781
4991·9	1	20027	07·0	1	20797
81·9	2	20067	03·3	1	20813
79·7†	1	20076	4796·2*	10	20844
76·7*	2	20088	92·8	2	20859
70·8	0	20112	91·1*	3	20866
69·0†	1	20119	89·8	1	20872
66·6†	1	20129	86·4	2	20887
58·2*	4	20163	84·5†	0	20895
55·0	1	20176	79·0	0	20919
51·3*	2	20191	77·0	1	20928
49·4†	1	20199	71·0	0	20954
46·4	0	20211	4767·4*	4	20970
42·5	1	20227	63·8	2	20986
38·1*	10	20245	59·9†	2	21003
30·8	1	20275	55·8	2	21021
29·6*	3	20280	49·7	1	21048
28·1*	1	20286	47·5*	3	21058
21·1	1	20315	43·2*	2	21077
11·7	0	20354	36·9	1	21105
07·1†	1	20373	33·1	2	21122
01·1	1	20398	30·6	1	21133
4899·4†	0	20405	27·5*	5	21147
94·1	0	20427	25·9	?	21154
91·5	0	20438	24·1*	2	21162
86·9†	4	20457	21·7	1	12173
81·2†	1	20481	16·1	1	21198
4872·9†	0	20516	14·1	1	21207

TABLE I (*Contd.*)

λ_{air}	I	$\nu_{vac.}$	λ_{air}	I	$\nu_{vac.}$
11·0	1	21221$_s$	81·4	0	21821
09·0	1	21230	79·6	2	21830
07·0	1	21239	75·6	0	21849
03·2	0	21256	4574·1	0	21856
00·1†	3	21270$_s$	72·4	2	21864
4697·9†	1	21280	69·7*	6	21877$_s$
96·0	1	21289	68·3	2	21884
93·7	0	21299	58·1	1	21933$_s$
85·8	0	21335$_s$	55·4	2	21946$_s$
83·8	1	21344$_s$	49·8*	5	21973$_s$
79·9*	7	21362$_s$	48·9	2	21977$_s$
77·7*	2	21372	46·0	1	21991
75·5	1	21382	44·1	2	22000
73·3	1	21392$_s$	42·3	0	22009
70·1	1	21407	40·0	1	22020
67·9	0	21417$_s$	38·2	1	22029$_s$
4666·1	1	21425$_s$	34·5	2	22047
64·2	0	21434$_s$	32·9†	3	22055
60·5*	4	21451$_s$	30·6	0	22066
59·0*	2	21458	28·3*	0	22077
57·0	2	21467	27·5*	1	22081
55·1*	3	21476$_s$	21·6	1	22110
53·3	1	21484	19·1	1	22122
51·2	1	21494	16·5	1	22135
47·7	1	21510	14·0	1	22147
43·2	0	21531	12·4	1	22155
40·6	1	21543	10·8	2	22163
37·8	1	21556$_s$	08·7*	3	22173
35·4	2	21567	06·9*	6	22182
34·3*	3	21572$_s$	4496·8	1	22232
32·6*	1	21580	94·5†	2	22243
31·6	2	21585	90·2	2	22265
29·8	0	21593	87·5†	1	22278
25·3	2	21614$_s$	85·9	1	22286
20·0	0	21639	84·1	1	22295
14·2*	6	21666$_s$	80·4	0	22313
13·0*	2	21672	72·8	0	22351
08·9	0	21691$_s$	71·2†	1	22359
06·6	1	21702$_s$	68·2*	2	22374
02·8	0	21720	65·6*	6	22387
4597·0	1	21747$_s$	60·8	1	22411
94·9*	2	21757$_s$	59·0†	2	22420
92·4	1	21769	56·5	1	22433
90·7†	2	21777	53·1	0	22450
82·3	1	21817$_s$	51·5	0	22458

TABLE I (*Contd.*)

λ_{air}	I	$\nu_{vac.}$	λ_{air}	I	$\nu_{vac.}$
47·7*	3	22477	67·5*	1	22890
36·5	1	22534	64·2*	1	22907
34·7	2	22543	58·5	2	22937
32·4†	1	22555	56·6*	1	22947
29·0*	2	22572	52·2*	2	22970
27·9	1	22578	46·0*	0	23003
25·9*	5	22588	40·8*	1	23031
23·9†	1	22598	38·1	0	23045
23·0	2	22603	36·8	1	23052
21·0	1	22613	34·2	0	23066
14·6†	0	22646	32·1†	0	23077
12·4	1	22657	20·5	0	23139
11·0*	2	22664	17·3*	0	23156
03·5*	0	22703	15·1	0	23168
01·3	0	22714	10·6	0	23192
4399·6*	2	22723	08·0†	2	23206
96·7	0	22738	4285·3	0	23329
94·0	0	22752	80·5	2	23355
92·6*	2	22759	79·3	0	23362
88·0*	2	22783	57·8	0	23480
4380·5	1	22822	51·8‡	2	23513
78·6*	0	22833	23·9	2	23668
75·3*	2	22849			

Note.—The bands marked with a suffix *g* are obtained from the plates taken in the first order of the 21-feet grating spectrograph. Others are obtained from the plates taken on the three-prism spectrograph.

The bands marked † are obtained also earlier by Ray and those marked by an asterisk mark are obtained by Ray as well as by Morgan. The band marked ‡ has also been recorded earlier by Morgan.

orders of a 21-feet grating spectrograph with a dispersion of 2·5 Å/mm. and 1·25 Å/mm. respectively. One to two hours' exposures were needed to record the spectrum on the three-prism glass spectrograph, whereas six hours were needed in the case of the 21-feet grating spectrograph. Measurements of the plates taken were carried out with a Zeiss Abbe Comparator.

VIBRATIONAL ANALYSIS

The wavelengths, wavenumbers and their visually estimated relative intensities of the band heads are given in Table I. The wavelengths of the intense bands are from plates taken on the I order of the 21-feet grating spectrograph while the others are obtained from the plates taken on the three-prism glass spectrograph. All the bands are clearly degraded to longer

wavelengths. The errors involved in the band heads may vary from ± 1 cm.$^{-1}$ for the bands recorded on the grating spectrograph to ± 3 cm.$^{-1}$ for the others. The agreement, between the measurements of all the bands observed in absorption and emission by the previous workers and those measured in the present experiment, shows clearly that the present system is the same as that observed by Morgan in absorption. The Deslandres scheme for the band system in the region 6170–4220 Å corresponding to the more abundant molecule $BiCl^{35}$ is given in Table II. All the bands could be fairly well represented within ± 4 cm.$^{-1}$ by the formula

$$\nu = 21757 + (217{\cdot}8\, v' - 2{\cdot}5\, v'^2 - 0{\cdot}02\, v'^3) - (307{\cdot}4\, v'' - 0{\cdot}96\, v''^2)$$

in which the same constants are being used as reported by Morgan and Ray except that a negative cubic term has been added for the upper state.

Isotopic Shifts

As the natural abundance ratio of Cl^{37} and Cl^{35} is 1 : 3, we expect two isotopic band heads of BiCl molecule namely, of $BiCl^{35}$ and $BiCl^{37}$ which will be having the intensity ratio of 3 : 1 respectively. The band heads which can be represented as isotopic components are listed in Table III, where the corresponding observed and calculated isotopic shifts are also included for comparison. Some of the bands which have been listed in Table III as belonging to $BiCl^{37}$ can also be represented as belonging to $BiCl^{35}$ with different v', v'' values and are, therefore, also shown as such in Tables II and III.

The agreement between the observed and calculated isotopic shifts from the present experiments as well as that observed in absorption by Morgan and Ray indicate clearly that this band system can, most probably, be attributed to the BiCl molecule.

The Dissociation Products and the Dissociation Energies of the States Involved

The present band system occurs in absorption as well as in emission. The very fact that the system has been observed in absorption shows that the lower state of the system is, most probably, the ground state of the BiCl molecule dissociating into Bi ($^4S_{3/2}$) + Cl ($^2P_{3/2}$) atoms which are the ground states of bismuth and chlorine atoms respectively. The dissociation energies of the upper and the lower states of the system cannot be determined accurately as the convergence limit of the system is not known. However, the linear extrapolation gives a value of $D_0 = 24614$ cm.$^{-1}$ for the lower state of the system which, as mentioned above, is probably the ground state

TABLE II

Vibrational scheme of the 6170–4220 Å system of BiCl

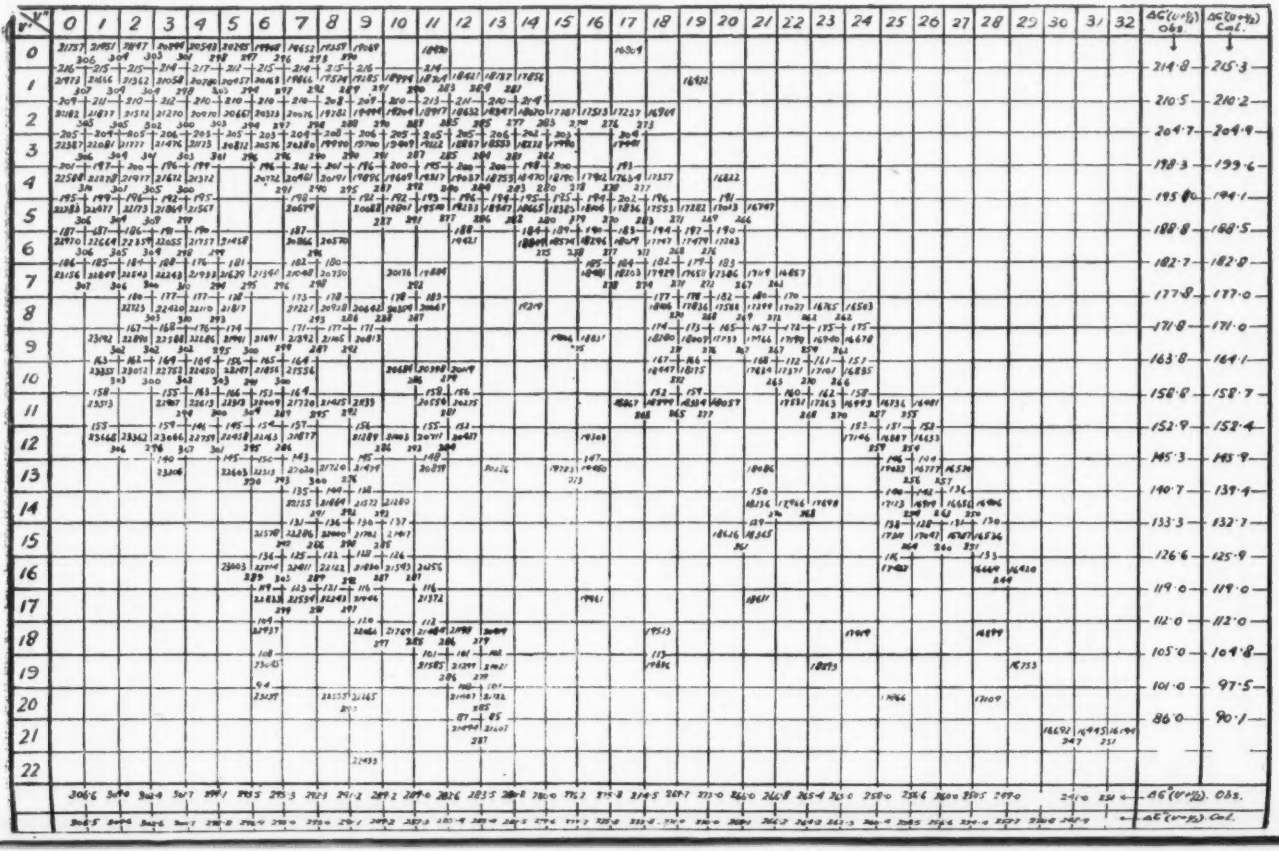

TABLE III

The probable isotopic shifts for the 6170–4220 Å system of BiCl

v', v''	ν in cm.$^{-1}$	I	$\Delta\nu$ in cm.$^{-1}$	v', v''	ν in cm.$^{-1}$	I	$\Delta\nu$ in cm.$^{-1}$
9, 24	16787	1	109	1, 13	18217	0	80
	16678	3	(111)		18137	2	(81)
11, 25	16844	1	108	7, 17	18284	0	81
	16736	2	(112)		18203	2	(80)
8, 23	16873	1	108	2, 13	18421	1	74
	16765	3	(109)		18347	2	(76)
7, 22	16964	1	107	5, 15	18460	2	75
	16857	3	(107)		18385	6	(76)
9, 23	17047	2	107	10, 18	18524	1	77
	16940	5	(106)		18447	2	(77)
2, 18	17073	1	105	4, 14	18544	2	74
	16964	1	(105)		18470	4	(74)
8, 22	17133	2	106	3, 13	18620	1	67
	17027	2	(104)		18553	3	(72)
15, 26	17158	0	111	6, 15	18646	0	72
	17047	2	(112)		18574	2	(72)
7, 21	17221	2	102	17, 21	18698	0	87
	17119	4	(102)		18611	1	(86)
12, 24	17250	1	104	5, 14	18736	2	71
	17146	1	(105)		18665	4	(70)
2, 17	17337	1	100	1, 11	18769	1	65
	17237	2	(99)		18704	3	(69)
8, 21	17396	1	97	4, 13	18818	1	65
	17299	4	(99)		18753	4	(68)
6, 19	17573	3	94	3, 12	18901	2	64
	17479	5	(94)		18837	5	(66)
1, 14	17940	0	84	2, 11	18983	1	66
	17856	1	(87)		18917	4	(64)
11, 20	18146	0	89	1, 10	19057	0	63
	18057	1	(86)		18994	2	(63)

TABLE III (*Contd.*)

v', v''	ν in cm.$^{-1}$	I	$\triangle\nu$ in cm.	v', v''	ν in cm.$^{-1}$	I	$\triangle\nu$ in cm.$^{-1}$
4, 12	19100	1	63	1, 7	19910	3	44
	19037	4	(62)		19866	7	(44)
9, 15	19171	?	65	4, 9	19934	1	38
	19106	1	(63)		19896	2	(43)
3, 11	19180	1	58	0, 6	19990	3	42
	19122	5	(60)		19948	5	(42)
2, 10	19260	2	56	3, 8	20027	1	37
	19204	3	(58)		19990	3	(41)
8, 14	19275	2	56	2, 7	20112	0	36
	19219	3	(60)		20076	1	(39)
1, 9	19340	1	55	2, 9	20129	1	41
	19285	4	(56)		20088	2	(40)
4, 11	19375	2	58	1, 6	20199	1	36
	19317	3	(56)		20163	4	(37)
0, 8	19415	1	56	7, 10	20211	0	35
	19359	2	(55)		20176	1	(39)
3, 10	19463	0	54	4, 8	20227	1	36
	19409	4	(54)		20191	2	(37)
2, 9	19545	4	51	0, 5	20280	3	35
	19494	6	(52)		20245	10	(35)
5, 11	19567	1	57	3, 7	20315	1	35
	19510	2	(52)		20280	3	(35)
1, 8	19623	2	49	2, 6	20405	0	32
	19574	8	(50)		20373	1	(33)
0, 7	19700	1	48	10, 11	20438	0	40
	19652	4	(49)		20398	1	(37)
2, 8	19830	1	48	4, 7	20516	0	35
	19782	3	(45)		20481	1	(31)
5, 10	19848	0	47	0, 4	20573	2	30
	19801	2	(46)		20543	8	(29)

TABLE III (*Contd.*)

v', v''	ν in cm.$^{-1}$	I	$\Delta\nu$ in cm.$^{-1}$	v', v''	ν in cm.$^{-1}$	I	$\Delta\nu$ in cm.$^{-1}$
11, 11	20586	1	30	0, 2	21162	2	15
	20556	1	(35)		21147	5	(15)
6, 8	20602	1	32	18, 12	21230	1	32
	20570	2	(30)		21198	1	(36)
2, 5	20693	1	26	8, 7	21239	1	18
	20667	3	(26)		21221	1	(17)
5, 7	20702	0	23	2, 3	21280	1	10
	20679	1	(27)		21270	3	(12)
7, 8	20772	1	22	5, 5	21280	1	10
	20750	2	(26)		21270	3	(14)
1, 4	20781	1	21	19, 12	21335	0	36
	20760	1	(24)		21299	0	(37)
4, 6	20797	1	25	1, 2	21372	2	10
	20772	1	(24)		21362	7	(10)
0, 3	20866	3	22	4, 4	21382	1	10
	20844	10	(22)		21372	2	(11)
6, 7	20887	2	21	9, 7	21407	1	15
	20866	3	(23)		21392	1	(14)
3, 5	20895	0	23	0, 1	21458	2	7
	20872	1	(22)		21451	4	(8)
8, 8	20954	0	26	6, 5	21467	2	9
	20928	1	(23)		21458	2	(10)
2, 4	20986	2	16	3, 3	21484	1	8
	20970	4	(19)		21476	3	(6)
5, 6	20986	2	16	18, 11	21510	1	26
	20970	4	(20)		21484	1	(26)
1, 3	21077	2	19	21, 21	21531	0	37
	21058	3	(17)		21494	1	(39)
11, 9	21154	?	21	2, 2	21580	1	8
	21133	1	(22)		21572	3	(6)

TABLE III (*Contd.*)

v', v''	ν in cm.$^{-1}$	I	$\Delta\nu$ in cm.$^{-1}$	v', v''	ν in cm.$^{-1}$	I	$\Delta\nu$ in cm.$^{-1}$
14, 9	21593	0	21	3, 0	22374	2	13
	21572	3	(18)		22387	6	(13)
19, 11	21614	2	29	4, 0	22572	2	16
	21585	2	(31)		22588	5	(17)
8, 5	21821	0	4	9, 3	22572	2	16
	21817	1	(4)		22588	5	(13)
16, 9	21849	0	19	13, 5	22598	1	5
	21830	2	(17)		22603	2	(7)
12, 7	21884	2	7	6, 1	22646	0	18
	21877	6	(8)		22664	2	(17)
15, 8	22009	0	9	8, 2	22703	0	20
	22000	2	(11)		22723	2	(17)
13, 7	22029	1	9	10, 3	22738	0	14
	22020	1	(7)		22752	0	(15)
6, 3	22047	2	8	5, 0	22759	2	24
	22055	3	(8)		22783	2	(21)
3, 1	22077	0	4	7, 1	22822	1	27
	22081	1	(6)		22849	2	(21)
16, 8	22135	1	13	6, 0	22947	1	23
	22122	1	(11)		22970	2	(24)
2, 0	22173	3	9	10, 2	23031	1	21
	22182	6	(8)		23052	1	(22)
7, 3	22232	1	11	9, 1	23168	0	24
	22243	2	(7)		23192	0	(26)
15, 7	22286	1	9	10, 1	23329	0	26
	22295	1	(5)		23355	2	(29)
6, 2	22351	0	8	11, 1	23480	0	33
	22359	1	(10)		23513	2	(31)

Note.—In the last column of the table under the heading $\Delta\nu$, the values given in brackets represent the calculated $\Delta\nu$ values and the others the observed $\Delta\nu$ values.

of the molecule. The present analysis of the band system gives a cubic term for the upper state which involves observed levels up to about $v' = 20$. The extrapolation involving the cubic term leads to a dissociation energy of $D_0' = 3750$ cm.$^{-1}$ for the upper state which will then dissociate at 25507 cm.$^{-1}$ One cannot attach much accuracy to these dissociation limits of the upper and lower states as these were obtained after fairly large extrapolations. However, it is to be noted that the difference between the two extrapolated dissociation limits 25507 cm.$^{-1}$ and 24614 cm.$^{-1}$ comes out to be 893 cm.$^{-1}$ which is quite close to the normal doublet separation of 881 cm.$^{-1}$ for the chlorine atom. Therefore, it appears quite likely that the dissociation limit of the upper state is not the same as that of the ground state but probably the next higher one with Bi ($^4S_{3/2}$) + Cl ($^2P_{1/2}$) atoms as the dissociation products. The next higher dissociation limit corresponding to Bi ($^2D_{3/2}$) + Cl ($^2P_{3/2}$) is expected to be at about 35910 cm.$^{-1}$ which is too high for the present upper state to dissociate into.

The reasons for taking Bi ($^4S_{3/2}$) + Cl ($^2P_{1/2}$) as the dissociation products for the upper state are the following:

The present analysis shows the position of the level with $v' = 18$ at 24855 cm.$^{-1}$ which has $\Delta G \simeq 104{\cdot}8$ cm.$^{-1}$ whereas the dissociation limit by linear extrapolation for the lower state is at 24614 cm.$^{-1}$ This value probably represents the maximum limit for D_0'' as the linear extrapolation for a non-ionic state is supposed to give a D_0 value higher than the actual one. If, however, the upper state is to dissociate at 24614 cm.$^{-1}$ a cubic term with a coefficient of about 0·07 has to be introduced whereas the analysis does not warrant such a high coefficient. Further it will be difficult to explain the observed isotopic shifts if another alternative analysis is chosen such that the upper state dissociates at 24614 cm.$^{-1}$

Acknowledgements

The authors wish to express their thanks to the Council of Scientific and Industrial Research for the sanction of a research scheme.

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EFFECT OF WINDOW ABSORPTION AND SOURCE BACKING ON β-SPECTRA

By B. N. Subba Rao

(*Tata Institute of Fundamental Research, Apollo Pier Road, Bombay*-1)

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(Communicated by Dr. B. V. Thosar, F.A.SC.)

Introduction

The distortive effects due to absorption and scattering of electrons in the counter window, in source backing and in the material of the source itself were noted quite early in the development of β-ray spectroscopy. It was by recognising these effects that the β-disintegration theory of Fermi was experimentally established by Lawson and Cork (1940), and Tyler (1939). With these facts in mind, very thin sources and source backings and also counter windows are employed in such work. These precautions only minimise the distortive effects, so that the true electron spectrum is obtained only if the correction factors for each of these sources of distortion are known. The part played by such and other effects in the study of shapes of β-spectra was discussed by Thosar (1958) and a survey of the earlier work was presented by Slätis (1958). The present work deals with an estimation of these correction factors and their application to the β-spectrum of Pm^{147}.

(*A*) *Window Absorption*

The effect of counter window absorption was studied in the intermediate image β-ray spectrometer using a thin source of Tl^{204} deposited on an aluminium backing (0·160 mgm./cm.^{2}) and using collodion films 0·060 to 0·960 mgm./cm.^{2} thick as counter windows. From the observed β-spectra, correction factors for window absorption were obtained in the conventional way. These could be represented by the formula,

$$f_w = e^{\mu x} \tag{1}$$

with

$$\mu = 1306\,(E - E_c)^{-2.1} \tag{2}$$

where electron energy E is in Kev. E_c is given in equation (3), and the mean surface density of the window (x) in mgm./cm.^{2} Due to uncertainties in the determination of low electron energy and intensity due to remanance effects

of the spectrometer and uncertainties in the thickness due to local density fluctuations, errors in these correction factors are estimated to be about 5% for electron energies above 10 Kev., and much larger for lower energies.

Corresponding to a window thickness x mgm./cm.^{2} there exists a minimum energy of electrons E_c Kev. at which transmission of electrons just starts. This is termed the cut-off energy. It is found that

$$x = 0{\cdot}007\, E_c^{1{\cdot}625}. \tag{3}$$

These determinations are in good agreement with those on low energy electrons (< 200 Kev.) by Schönland (1925) and others (Slätis, 1955).

The mean angle (θ) of incidence of the electron beam was, in the present case, about 45°. Neglecting the small contribution from large angle scattering in collodion (considered for the present treatment as essentially Carbon and Hydrogen) to these correction factors, one can generalize the above formulæ (1) and (3) so as to be applicable for any spectrometer geometry with a mean angle of incidence, θ, of the electron beam in the form

$$f_w = \exp.\ [900\,(E - E_c)^{-2{\cdot}1}\, x\, (\cos\theta)^{-1}] \tag{4}$$

and

$$x = 0{\cdot}01\, E_c^{1{\cdot}625} \cos\theta \tag{5}$$

These relations are applicable for $E < 200$ Kev. and $x < 1$ mgm./cm.^{2}

(*B*) *Backscattering*

Though many workers have observed the effect of backscattering, correction factors to the electron spectrum have not been quantitatively determined except for integral β-spectra with very different maximum energies and orders of forbiddenness. On the theoretical side, the multiplicity and variety of processes that contribute to backscattering has made it very difficult to obtain accurate expressions by means of which corrections for such effects may be derived.

In this work, the effect of backscattering was studied using a thin source of Tl^{204}, a counter window 0·1 mgm./cm.^{2} thick and aluminium source backings from 0·2 to 2 mgm./cm.^{2} thick. Defining the ratio of the number of electrons observed with backscattering to those without backscattering as the backscattering factor, the relationship between backscattering factor p, and backing thickness for various electron energies are presented in Fig. 1. From these curves correction factor f_b for backscattering at any backing thickness and any electron energy in the range of 20 to

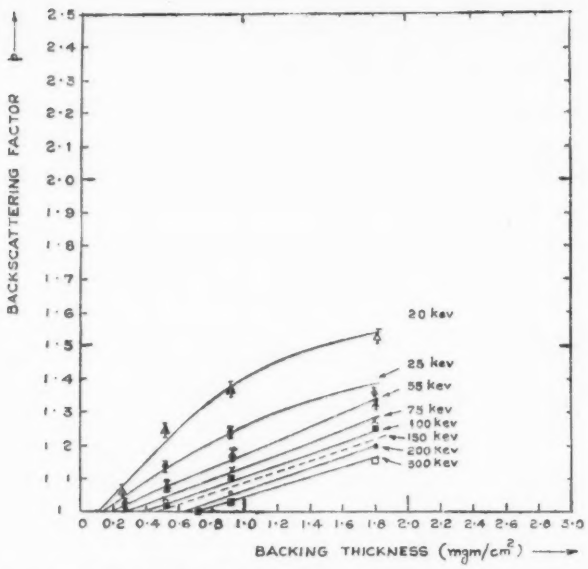

FIG. 1. Backscattering of low energy electrons in thin aluminium.

300 Kev. may be obtained as reciprocals of p. The observations below 20 Kev. are much affected in accuracy due to uncertainties in the determination of low electron energy and electron intensity as pointed out in Section A and due to errors in determining the intensity of electrons at zero backing thickness.

Bothe (1933) has discussed the experimental observations on backscattering, or more precisely, backdiffusion. Accordingly, backscattering should increase with increasing thickness of the scatterer until after a certain thickness, which depends on electron energy and the scattering material, it reaches a saturation value. This saturation backscattering factor is itself found to be little energy dependent but strongly dependent on the coulomb field of the scattering nucleus. In the present case, 1·8 mgm./cm.² does not appear to provide saturation backscattering thickness for electron energy greater than 25 Kev. The new feature observed in these curves (Fig. 1) is the intercept on the axis of backing thickness. This implies that backscattering is initiated, as it were, at a minimum backing thickness. Denoting this scatter-initiating thickness by t_0 (mgm./cm.²), it was found that

$$t_0 = 0{\cdot}0110\, E^{0,755} \qquad (E \leqslant 300 \text{ Kev.}) \tag{6}$$

This expression should be quite useful in estimating the backing thickness which may be employed without appreciable backscattering contribution for electrons of energy above E Kev. The error in t_0 is estimated to be about 10% for electron energy greater than 20 Kev.

Experimental evidence (Bothe, 1933) indicates that backscattering, particularly before backdiffusion stage is reached, is essentially due to large angle coulomb scattering of incident electrons by nuclei. So, the cross-section for such a process, in ideal single scattering approximation, is given by the well-known Rutherford's formula,

$$\frac{d\sigma}{d\Omega} = \frac{Z^2 e^4}{16 E^2} \frac{1}{\sin^4 \frac{\theta}{2}}. \qquad (7)$$

It follows that for a given energy and large angle scattering, the cross-section for backscattering is relatively much larger in heavier elements than in lighter ones. For light elements, like aluminium under consideration, due to the low cross-section for large angle scattering, electrons of this range should traverse a finite thickness of the scattering material before having a good chance of being backscattered. This is what has been observed in this work and called the scatter-initiating thickness. It may now be seen that this thickness should vary inversely as the cross-section for large angle scattering. In materials like gold and lead, the probable thickness that low energy (< 300 Kev.) electrons traverse before being backscattered should be of the order of a few atomic layers. When comparatively thick scatterers and electrons of a continuous range of energy are involved, this scatter-initiating thickness is obscured. This is what appears to have happened in earlier works.

It may be noted that the geometry of acceptance in this β-ray spectrometer and the interscattering between the layer of source material and source backing play a very important role in the backscattered electron distribution, referred to here. These results on backscattering are applicable to the geometry found in the intermediate image β-ray spectrometer.

(*C*) *Application to the β-Spectrum of* Pm^{147}

Correction factors determined in the way described above have been applied to the non-unique first forbidden β-spectrum of Pm^{147}, which was shown by Langer (1950) and Maize and Zaffrano (1953) to have a straight line Kurie plot down to about 10 Kev.

A thin source of Pm^{147} deposited by evaporation on to an aluminium backing ($\cdot 750$ mgm./cm.^{2}) was used to observe the β-spectrum. The Geiger

counter window of collodion was 0·080 mgm./cm.^{2} thick. In view of nearly 6% uncertainty in backscattering correction factors, observed points at electron energies greater than 100 Kev. where these correction factors are $\geqslant 0{\cdot}95$, are not corrected.

The Kurie plot as observed (curve A), after being corrected for absorption in the counter window using correction factors discussed above (curve B), and after correcting for backscattering effects also (curve C), using the data presented in Fig. 1, are shown in Fig. 2.

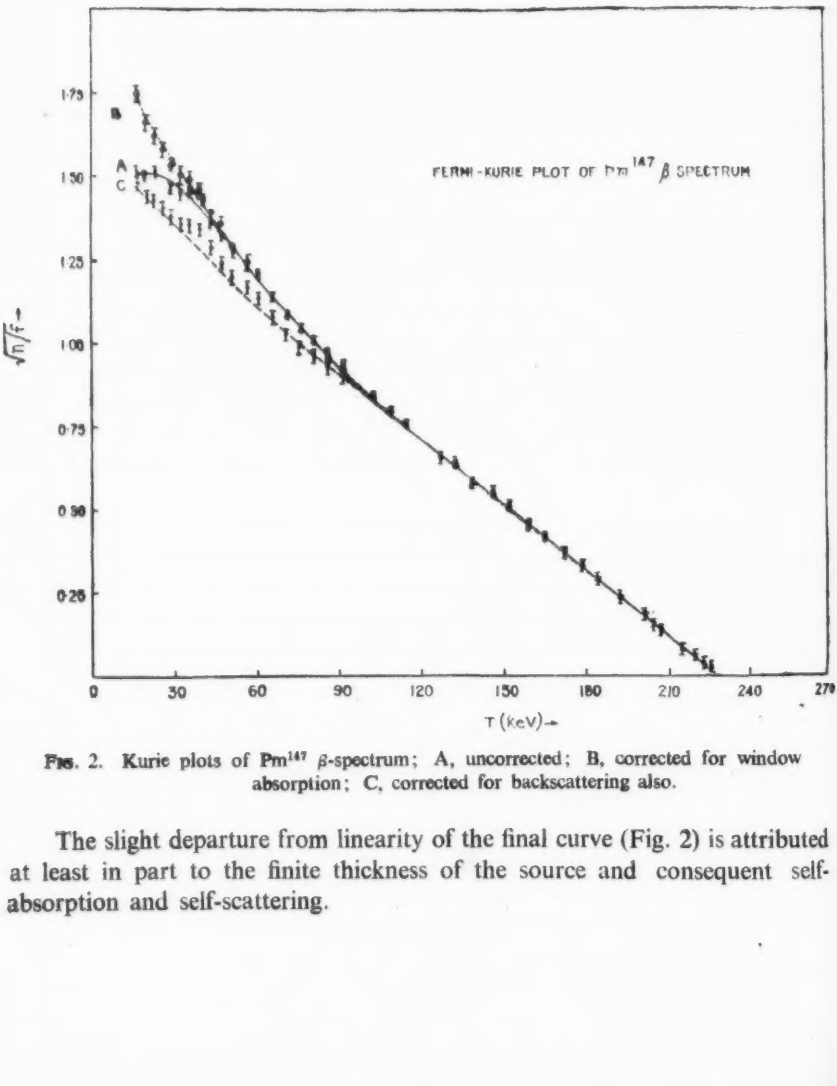

Fig. 2. Kurie plots of Pm^{147} β-spectrum; A, uncorrected; B, corrected for window absorption; C, corrected for backscattering also.

The slight departure from linearity of the final curve (Fig. 2) is attributed at least in part to the finite thickness of the source and consequent self-absorption and self-scattering.

Note added in Proof:

Recently Gubernator and Flammersfeld (*Zeit. Phys.*, 1959, 156, 179) have found a formula for absorption of low energy electrons in various materials. In the notation of the present work, it may be written as $E_c = 14 \cdot 3\,(Z^{4/3}/A)\; x^{0.61}$. Considering the probable formula, $C_6H_5O_9N_2$ for collodion, equation (5) can be rewritten as $E_c = 15\;(Z^{4/3}/A)\; x^{0.615}$ Due to lack of knowledge of the accurate formula for collodion, the two observations should be considered to be in agreement.

Summary

Estimates of the distortive effects of window absorption and backscattering from source backings on β-spectra are presented as observed in the intermediate image β-ray spectrometer. The existence of a scatter-initiating thickness is pointed out and explained. These correction factors are applied to the β-spectrum of Pm^{147} to estimate their validity.

Acknowledgement

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POLAROGRAPHIC ESTIMATION OF CADMIUM IN PRESENCE OF NICKEL, COBALT AND BISMUTH

By H. C. Saraswat

(Department of Chemistry, Christ Church College, Kanpur)

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Introduction

Quantitative estimation of cadmium has attracted the attention of numerous workers in recent years. Gardiner and Regers[1] made use of stationary mercury plated platinum electrode for determination of sub-micrograms of Cd^{2+} and Zn^{2+}. Dithizone was used for estimation of Cd^{2+} colorimetrically in presence of other interfering metals.[2] Adams[3] titrated Cd^{2+} with ethylenediaminetetraacetic acid (EDTA) using controlled current technique. Cadmium in presence of Zn^{2+} in sodium hydroxide solution was estimated spectrophotometrically with EDTA.[4] The principle of coulogravimetric analysis was found useful[5] for the determination of Zn^{2+} and Cd^{2+}. Traces of Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} in rocks were also determined polarographically by using rubeanic acid and 1-nitroso-2-naphthol.[6] Nobu-Yuki Tanaka and others[7] carried out amperometric and potentiometric titrations of Cd^{2+} with EDTA in acetate buffers (pH 4·2) using dropping mercury electrode (d.m.e.). Silve Kallamanu and co-workers[8] determined Cd^{2+} and Zn^{2+} by separating them from each other and also from other metals by anion-exchange resins. Kohnt[9] developed a method for separation of Cd^{2+} from a mixture of Cd^{2+} and Bi^{3+} by means of KI, and estimated Cd^{2+} using hydrazone hydroxide. Sandberg[10] used naphthaquinoline in sulphuric acid for titrating Cd^{2+} amperometrically. Author's earlier work[11] indicated that Cd^{2+} in pure solutions could be estimated amperometrically using $K_4Fe(CN)_6$ as the titrating agent. The present communication describes a simple amperometric method for estimation of Cd^{2+} in mixtures of Cd^{2+} with Ni^{2+}, Co^{2+}, Bi^{3+}, etc.

Experimental

In all experiments reported in the present communication, systems containing pure substances only were examined. The following substances of AnalaR B.D.H. grade were used:

(i) Cadmium sulphate was recrystallised in double distilled water and dried in vacuum. The solutions prepared were standardized by gravimetric method using pyridinethionate.[12]

(ii) Nickel sulphate was recrystallised and dried at 50° C. The exact concentration of Ni^{2+} was estimated gravimetrically using dimethylglyoxime.[12]

(iii) Cobalt sulphate was recrystallised and dried. Gravimetric method using 1-nitroso 2-naphthol was employed for standardisation of cobalt solution.

(iv) Bismuth nitrate was of B.D.H. pure quality and was used without further purification.

(v) Potassium ferrocyanide (B.D.H. AnalaR). Solutions of this substance were standardised against standard solutions of $Pb(NO_3)_2$ prepared from recrystallised and dried substance.

(vi) Potassium chloride and potassium citrate (B.D.H. AnalaR) were used without further purification, as supporting electrolytes.

The polarograph employed in the present investigation was of manual type and assembled in this laboratory. The following were the characteristics of the capillary used:

Mass of the drop	..	..	0·719 mg.
Time	..	..	4·1 sec.

Results and Discussion

In the first series of experiments polarograms of Cd^{2+} in 1 M KCl solution were obtained to examine the accuracy of the assembled polarograph. The half-wave potential of Cd^{2+} corresponded to $-0{\cdot}635$ volts *vs.* S.C.E. in close agreement with the data reported in the literature.[13] Further, the observed limiting current i_d was in accord with the value calculated from Ilkovic's equation[13]:

$$i_d = 605\, n\, D^{\frac{1}{2}} C\, m^{\frac{2}{3}}\, t^{\frac{1}{6}}$$

where i_d is the limiting current in microamperes; n, the number of electrons involved in the reduction process; D, the diffusion coefficient (cm.^{2} sec.$^{-1}$); and t, the average life of the drop (sec.). Polarograms obtained with Ni^{2+}, Co^{2+} and Bi^{3+} solutions also gave data which could be compared well with the results of earlier workers.[13] Further, the values of i_d attained saturation for all the reducible ions reported here, at and above 1·6 volts *vs.* S.C.E., at these potentials. i_d values were proportional to the concentration over a

limited range ($\leqslant 15$ mM.). All amperometric titrations reported below were carried out at $-1{\cdot}80$ volts.

Figure 1 gives results on amperometric titration of cadmium solutions against $K_4Fe(CN)_6$, in presence of potassium citrate as the supporting electrolyte. In accord with earlier data[11] obtained with KCl as the supporting electrolyte, Cd^{2+} could be estimated amperometrically using $K_4Fe(CN)_6$ in presence of K.Cit. The end-points as indicated in Fig. 1 were sharp, and the experiment inaccuracy was of the order of $\pm 0{\cdot}5$ per cent. (*see* Table I). Unlike at lower concentrations Curves 1–3 (Fig. 1), the decrease in i_d at higher concentrations of Cd^{2+} (Curves 4–6) was not linear with the volume of the titrant; this appears to be due to the limitation in the applicability of Ilkovic's equation to higher concentrations of the reducible ion.

Figures 2–4 give amperometric curves representating the estimation of Cd^{2+} in presence of Ni^{2+}, Co^{2+} and Bi^{3+} respectively, using KCl and K.Cit.

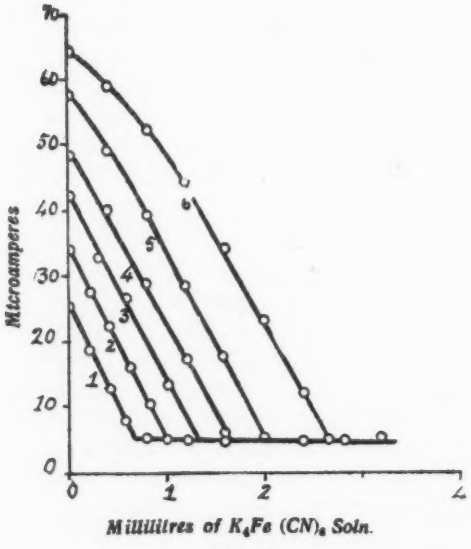

FIG. 1

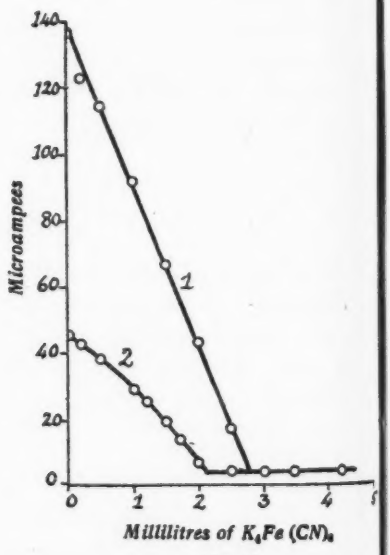

FIG. 2

FIG. 1. Amperometric titration of Cd^{2+} against $K_4Fe(CN)_6$. Curves 1–6 refer to 10, 15, 20, 25, 30 and 40 mM. of Cd^{2+}. Supporting electrolyte—M/2 K.Cit.

FIG. 2. Determination of Cd^{2+} in presence of Ni^{2+}. Concentration of $K_4Fe(CN)_6$ = 300 mM.; of Cd^{2+} = 30 mM.; of Ni^{2+} = 10 mM. Curve 1 refers to KCl and 2, to K.Cit. used as supporting electrolytes.

TABLE I

Amperometric titration of cadmium by potassium ferrocyanide

Strength of $K_4Fe(CN)_6$ = 300 mM.
Supporting electrolyte = M/2 K.Cit.

Concentration of $CdSO_4$ Soln. in mM.	Volume of $K_4Fe(CN)_6$ in ml.	
	Required	Observed
10	0·675	0·670
15	1·00	1·00
20	1·35	1·33
25	1·65	1·67
30	2·03	2·00
40	2·63	2·66

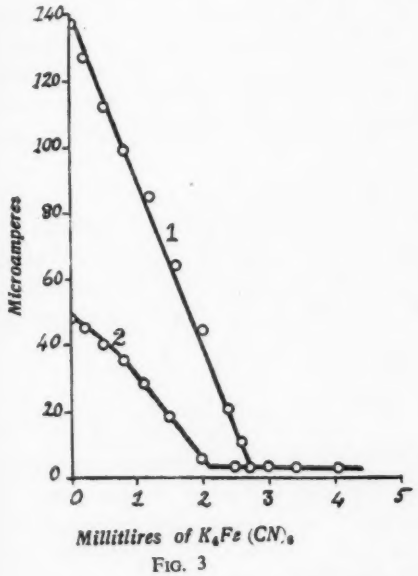

FIG. 3

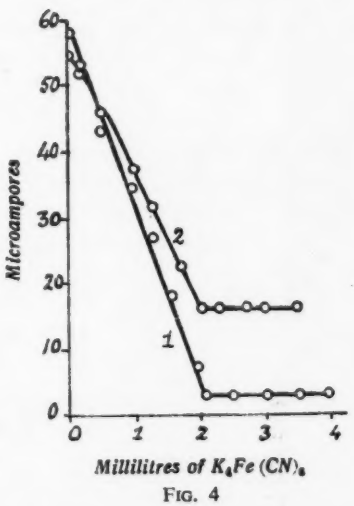

FIG. 4

FIG. 3. Estimation of Cd^{2+} in presence of Co^{2+}. Concentration of $K_4Fe(CN)_6$ = 300 mM; of Cd^{2+} = 30 mM.; of Cd^{2+} = 10 mM. Curve 1 refers to KCl, and 2, to K.Cit. as supporting electrolytes.

FIG. 4. Determination of Cd^{2+} in presence of Bi^{3+}. Concentration of $K_4Fe(CN)_6$ = 300 mM; Supporting electrolyte — M/2 K.Cit. Curve 1 refers to estimation of Cd^{2+} and 2, to a mixture of Cd^{2+} and Bi^{3+}.

as supporting electrolytes. In all the series of experiments, a mixture of $Cd^{2+} + Ni^{2+}$, $Cd^{2+} + Co^{2+}$ or $Cd^{2+} + Bi^{3+}$ was titrated against standard solution of $K_4Fe(CN)_6$; Curve 1, Figs. 2–4, refer to KCl, while Curve 2, to K.Cit. as the supporting electrolyte. It is of interest to note that while the amperometric Curve 1, Figs. 2–4 give end-points corresponding to the total amount of $Cd^{2+} + Ni^{2+}$, $Cd^{2+} + Co^{2+}$ or $Cd^{2+} + Bi^{3+}$, Curve 2 indicates only the amount of Cd^{2+}. In other words, the presence of Ni^{2+}, Co^{2+} or Bi^{3+} interferes the amperometric estimation of Cd^{2+} in KCl solutions using $K_4Fe(CN)_6$ as the titrating agent; and does not do so in K.Cit. medium. Cadmium could be determined with accuracy in citrate solutions even in the presence of all the three metallic components, *viz.*, Ni^{2+}, Co^{2+} and Bi^{3+} (*see* Fig. 5). This observation is clearly demonstrated by the data in Fig. 6. In this, Curve 1 refers to amperometric tiration of 30 mM. of Cd^{2+} alone in

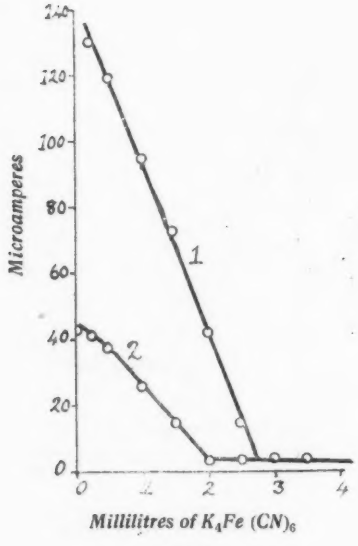

FIG. 5

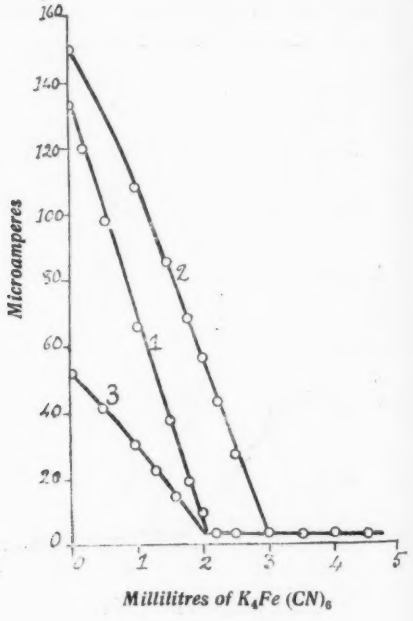

FIG. 6

FIG. 5. Estimation of Cd^{2+} in presence of Ni^{2+}, Co^{2+}, etc. Curve 1 refers to amperometric titration of 30 mM. of Cd^{2+} + 5 mM. of Ni^{2+} + 5 mM.; of Co^{2+} in KCl; and 2, to the titration of the same mixture in K.Cit. medium.

FIG. 6. Role of K.Cit. in amperometric estimation of Cd^{2+} in presence of Ni^{2+}, Co^{2+} and Bi^{3+}. Curve 1 refers to amperometric estimation of 30 mM. of Cd^{2+} in KCl; 2, of 30 mM. of Cd^{2+} + 15 mM. of Ni^{2+} in KCl; 3, of 30 mM. of Cd^{2+} + 15 mM of Ni^{2+} in K.Cit. medium.

KCl solution; Curve 2 refers to the same of a mixture of 30 mM. of Cd^{2+} and 15 mM. Ni^{2+} in 1 M KCl solution. The shift of the end-point by 1·9 c.c. of the titrant *vs.* $K_4Fe(CN)_6$ corresponding to the amount of Ni^{2+} in the mixture could be noticed. Instructive was the observation that when the same mixture of Cd^{2+} and Ni^{2+} was titrated against $K_4Fe(CN)_6$ in potassium citrate solution (Curve 3, Fig. 6) the end-point corresponded to the same as in Curve 1, referring to the amount of Cd^{2+} alone.

The non-interference of the presence of Ni^{2+}, Co^{2+} and Bi^{3+} in the amperometric estimation of Cd^{2+} using $K_4Fe(CN)_6$ as the titrating agent and K.Cit. as the supporting electrolyte suggest that the citrate complexes of Co^{2+}, Ni^{2+} and Bi^{3+} are more stable than the corresponding ferrocyanides. Knowledge on the stability constants of the ferrocyanide complexes of the metallic constituents is not available in the literature.

Summary

Cadmium was estimated amperometrically using $K_4Fe(CN)_6$ as titrating agent, with an experimental inaccuracy of $\pm$ 0·5 per cent. In citrates employed as supporting electrolyte for the reduction at d.m.e. of Cd^{2+}, the presence of Ni^{2+}, Co^{2+} and Bi^{3+} did not interfere with the estimation, due to the formation of more stable citrate complexes of Ni^{2+}, Co^{2+} and Bi^{3+} than the corresponding ferrocyanide complexes.

Acknowledgement

Author's thanks are due to Dr. N. A. Ramaiah, Head of the Department of Physical Chemistry, National Sugar Institute, Kanpur, for his valuable discussions and encouragement during the work; and to Mr. N. Abraham, Principal, Christ Church College, for his interest in the work.

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HETEROCYCLIC COMPOUNDS, PART XV*

Synthesis of α-Pyridylindoles

BY V. K. LAKSHMANAN

(Department of Organic Chemistry, University of Madras, Madras-25)

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(Communicated by Dr. K. N. Menon, F.A.SC.)

ALSTYRINE,[1] an important degradation product of a number of indole alkaloids, is characterised by the presence of α-pyridylindole ring system. Ever since the total synthesis of alstyrine was accomplished by Swan,[2] the chemistry and synthesis of substituted, as well as unsubstituted, α-pyridylindoles has engaged the attention of a number of workers. The present investigation had as its objective the synthesis of some of the methyl-substituted α-pyridylindoles by the obvious application of the Fischer indole reaction, with methyl groups in the various positions of the benzene ring.

This work also records the comparative efficacy of the following reagents to effect the Fischer ring closure, in the present work.

(1) Orthophosphoric acid (Sp. Gr. 1·75).

(2) Ethanolic hydrogen chloride.

(3) Polyphosphoric acid.

The indoles prepared in the present investigation can be conveniently classified as follows:—

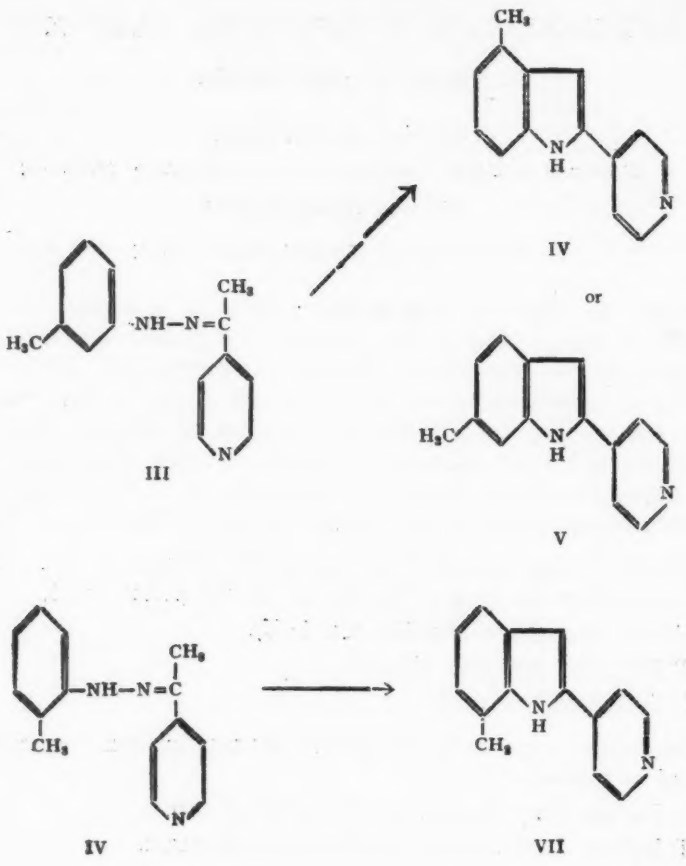
(1) Indoles from 4-acetyl pyridine-tolylhydrazones.

(2) Indoles from 2-acetyl pyridine-tolylhydrazones.

1. *Indoles from 4-acetyl pyridine-tolylhydrazones*

I II

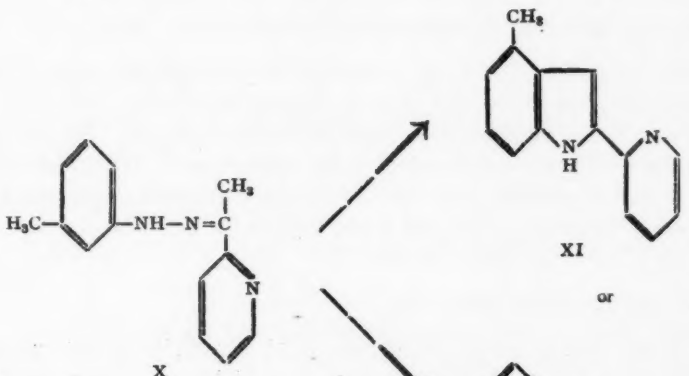
*Part XIV, *Proceedings*, 1959, Vol. XLIX, No. 1, Sec. A, p. 31.



4-Acetyl pyridine-*p*-tolylhydrazone (I) from 4-acetyl pyridine,[3] on treatment with orthophosphoric acid, cyclized to give 2-(4′-pyridyl)-5-methyl indole (II). The ring closure of 4-acetyl pyridine-*m*-tolylhydrazone (III) was also effected with polyphosphoric acid. In this case the indole obtained may be either 2-(4′-pyridyl)-4-methyl indole (IV) or 2-(4′-pyridyl)-6-methyl indole (V). The proof of rigid structure has not been attempted in the present work. When an attempt was made to cyclize 4-acetyl pyridine-O-tolylhydrazone (VI) in the presence of ethanolic hydrogen chloride, the hydrazone was recovered unchanged. However it was successfully ring-closed to 2-(4′-pyridyl)-7-methyl indole (VII), with ploy phosphoric acid.

2. *Indoles from 2-acetyl pyridine tolylhydrazones*

VIII IX



X XI or XII

XIII XIV

2-(2′-pyridyl)-5-methylindole (IX).

2-(2′-pyridyl)-4-or-6-methyl indole (XI or XII),

2-(2′-pyridyl)-7-methyl indole (XIV).

The above three indoles were obtained by cyclizing respectively, *p*-, *m*-, and O-tolylhydrazones of 2-acetyl pyridine.

Of all three reagents employed for Fischer ring closure in the present investigation, polyphosphoric acid was found to be the most effective one. The superiority of polyphosphoric acid consists in that it produces much purer products in better yield and in lesser reaction period.

EXPERIMENTAL

*4-Acetyl pyridine-*p*-tolylhydrazone (I)*

4-Acetyl pyridine[3] (3 g.) in alcohol (15 ml.) was added to *p*-tolylhydrazine (3 g.), dissolved in alcohol (15 ml.), the mixture was allowed to stand overnight and then refluxed on a water-bath for an hour and a half. The hot solution was diluted with water and cooled in the refrigerator. The hydrazone separated as yellow needles, m.p. 140°; yield 5 g. The hydrazone could not be obtained in analytical purity and it was used in the next step without purification.

2-(4′-pyridyl)-5-methyl indole (II)

4-Acetyl pyridine-*p*-tolylhydrazone (4 g.) was added to orthophosphoric acid (40 ml.; sp. gr. 1·75) contained in a 100 ml. round-bottomed flask. The contents were heated on a water-bath for two hours with exclusion of moisture. The flask was cooled and the solution was poured over cracked ice. It was basified with solid sodium bicarbonate and left overnight in the ice-chest. The indole, which separated as an yellow solid, was collected and crystallised from methanol, m.p. 239°; yield 2 g. Found: N = 13·74. $C_{14}H_{12}N_2$ requires N = 13·46.

The picrate, crystallised from acetic acid in the form of red needles, m.p. 256° (decomp.). Found: N = 15·82. $C_{14}H_{12}N_2 \cdot C_6H_3N_3O_7$ requires N = 16·01.

*4-Acetyl pyridine-*m*-tolylhydrazone (III)*

This hydrazone was prepared from *m*-tolylhydrazine (3 g.) and 4-acetyl pyridine (3 g.) had m.p. 165°; yield 3·4 g.

2-(4′-pyridyl)-4-or-6-methyl indole (IV or V)

The crude hydrazone (3·4 g.) was added to polyphosphoric acid prepared from orthophosphoric acid (6 g.) and phosphorus pentoxide (10 g.).

The mixture was stirred with a thermometer by hand and gradually heated in an oil-bath until the internal temperature reached 120°. It was left at this temperature for 3 minutes. Then the flask was cooled and the contents diluted with water. The difficultly soluble phosphate was washed with concentrated hydrochloric acid to facilitate solubility. The clear solution was treated with charcoal, filtered and basified with 20% sodium hydroxide solution. The base, which separated immediately, was collected and dried. It crystallised from methanol in colourless needles, m.p. 280°, yield 2·5 g. Found: N = 13·26. $C_{14}H_{12}N_2$ requires N = 13·46.

The picrate crystallised from methanol in red plates, m.p. 270° (decomp.). Found: N = 15·88. $C_{14}H_{12}N_2 \cdot C_6H_3N_3O_7$ requires N = 16·01.

4-Acetyl pyridine O-tolylhydrazone (VI)

O-tolylhydrazine (3 g.) and 4-acetyl pyridine (3 g.) gave the hydrazone, m.p. 95°; yield 3·3 g.

2-(4'-pyridyl)-7-methyl indole (VII)

The following three methods have been attempted for the synthesis of this indole.

1. The hydrazone VI was cyclized in the presence of orthophosphoric acid to give the indole. But, it was obtained in a highly impure condition and could not be crystallised from any common organic solvent.

2. An unsuccessful attempt made to ring-close the hydrazone by the influence of ethanolic hydrogen chloride resulted only in the production of the hydrochloride of the hydrazone.

3. 4-Acetyl pyridine-O-tolylhydrazone (VI) (3 g.) was added to polyphosphoric acid. The mixture was gradually heated in an oil-bath until the internal temperature reached 140°. It was kept at this temperature for 2–3 minutes and then cooled and diluted with water. When concentrated hydrochloric acid was added to dissolve the difficultly soluble phosphate, the beautiful yellow hydrochloride of the indole separated instantaneously. The hydrochloride was collected and dissolved in hot water. The yellow solution was cooled and basified to give the corresponding indole. It crystallised from dilute methanol in colourless needles, m.p. 187°; yield 1·5 g. Found: N = 13·31. $C_{14}H_{12}N_2$ requires N = 13·46.

The picrate crystallised from alcohol in red plates, m.p. 284° (decomp.). Found: N = 15·76. $C_{14}H_{12}N_2 \cdot C_6H_3N_3O_7$ requires N = 16·01.

2-Acetyl pyridine-tolylhydrazone (*VIII*)

This hydrazone was obtained as a brown viscous liquid when 2-acetyl pyridine[4] (3 g.) was reacted with *p*-tolylhydrazine (3 g.). The crude compound weighed 4 g.

2-(2'-pyridyl)-5-methylindole (*IX*)

The above crude hydrazone (4 g.) underwent a Fischer ring closure when it was treated with orthophosphoric acid (40 ml.). The indole obtained was crystallised from methanol, m.p. 131°; yield 1 g. Found: N = 13·04. $C_{14}H_{12}N_2$ requires N = 13·46.

The picrate crystallised from acetic acid in the form of yellow needles, m.p. 229° (decomp.). Found: N = 16·00. $C_{14}H_{12}N_2.C_6H_3N_3O_7$ requires N = 16·01.

2-Acetyl pyridine-O-tolylhydrazone (*XIII*)

The above hydrazone was obtained when 2-acetyl pyridine (3 g.) was condensed with O-tolylhydrazine (3 g.), m.p. 65°; yield 4 g.

2-(2'-pyridyl)-7-methyl indole (*XIV*)

This indole was obtained when the hydrazone XIII (4 g.) was treated with polyphosphoric acid. The indole crystallised from dilute methanol in colourless needles, m.p. 110°; yield 1·5 g. Found: N = 13·62. $C_{14}H_{12}N_2$ requires N = 13·46.

The picrate crystallised from alcohol in red needles, m.p. 260° (decomp.). Found: N = 16·35. $C_{14}H_{12}N_2.C_6H_3N_3O_7$ requires N = 16·01.

2-Acetyl pyridine-m-*tolylhydrazone* (*X*)

This hydrazone was obtained from 2-acetyl pyridine (3 g.) and *m*-tolylhydrazone (3 g.), m.p. 105; yield 3 g.

2-(2'-Pyridyl)-6-or-4-methyl indole (*XI or XII*)

The above hydrazone was ring-closed with polyphosphoric acid. The indole (XI or XII) crystallised from methanol in colourless needles, m.p. 147°; yield 1·5 g. Found: N = 13·52. $C_{14}H_{12}N_2$ requires N = 13·46.

The picrate crystallised from acetic acid in yellow needles, m.p. 244° (decomp.). Found: N = 15·97. $C_{14}H_{12}N_2.C_6H_3N_3O_7$ requires N = 16·01.

SUMMARY

Synthesis of six α-pyridylindoles is reported.

Acknowledgement

I wish to thank Dr. K. N. Menon for his valuable help and guidance and the Government of Madras for a scholarship.

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